CHEMICAL MONITORING

8 Chemical Tests

Many types of chemical tests can be performed to assess varying aspects of stream water quality. However, volunteer monitoring programs are faced with both financial and technical limitations. Given these constraints, Hoosier Riverwatch trains volunteers to conduct eight of the chemical tests considered by the National Sanitation Foundation and *The Field Manual for Global Low-Cost Water Quality Monitoring* (Mitchell and Stapp, 1997) to be most useful in determining stream water quality:

Dissolved Oxygen E. coli

pH Water Temperature Change

Biochemical Oxygen Demand (5-Day)

Phosphates (Ortho and Total)

Nitrates

Turbidity

Riverwatch Chemical Testing Instructions

Hoosier Riverwatch does not require volunteers to use a standard set of equipment or methods for chemical testing. However, the majority of volunteer groups actively participating in the program have received equipment through Riverwatch grants. The chemical testing instructions presented in this chapter are for the most common methods used by volunteer stream monitoring groups in Indiana. They are also the methods presented during Riverwatch training sessions.

The methods are separated into two sections: Standard Chemical Testing Instructions and Advanced Chemical Testing Instructions. Standard Chemical Testing includes the use of the GREEN Standard Water Monitoring Kit. Advanced Chemical Testing includes the use of the HACH Stream Survey kit, Coliscan Easygel (for *E.*coli), and a turbidity tube. Detailed background information on each of the parameters is provided in the Advanced Chemical Testing section.

Hints For Performing Chemical Tests

- ✓ Read all of the instructions for each test before you perform the procedures.
- ✓ Do not store the Hach or GREEN chemical testing kits in your car or in any extreme temperatures.
- ✓ **Practice!** The more familiar you are with the tests, the easier they will be to perform, and the more accurate your results will be.
- ✓ Perform each procedure three times to assure precision and accuracy in your results.
- ✓ Wear protective gloves and safety goggles. Do not wear sunglasses when reading the test results.
- ✓ Rinse collection tubes or bottles with *sample* water before collecting the sample.
- ✓ Rinse testing tubes and bottles with *distilled* water after completing each test.
- ✓ Clean glassware with non-abrasive detergents or a solvent such as isopropyl alcohol. Use a soft cloth for wiping or drying. Do not use paper towels or tissue on plastic tubes as they may scratch.
- ✓ Wash your hands when you are finished.
- ✓ Obtain your water sample from the stream's main stream flow (usually in the middle). Take the sample 3-5 inches under the surface. See Figure 11 and more tips on the next page!

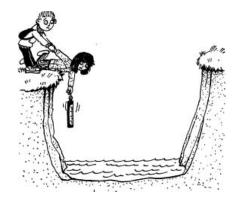
Tips on Collecting Water Samples

How you physically obtain the water sample depends on the size, depth, and banks of your stream. Most Hoosier Riverwatch volunteers sample wadeable streams. If you are wading, make sure that you collect water from a point upstream of where you are standing, being careful not to stir up any sediment. The sample must be collected in a clean container to avoid contamination. Collecting water directly from the stream with the container used for the chemical test is preferred.

Deep water or steep banks are dangerous (see Figure 11 below). Depending upon conditions at your site, you may need to use alternative sampling techniques. If you have a bridge at the site, you may be able to lower a sampling container or bucket down to the stream. At some sites, you may be able to sample with a rod (cup on a stick) from the edge of the stream. Regardless of the method of collection, sample water should be collected from the **main stream flow**.

Rinse your container three times with river water before collecting your final sample. Lower your container down 3 to 5 inches below the surface of the water so that your sample is representative of the whole stream.

Figure 11





Pictures from GLOBE 1997.

How to Discard Chemical Waste

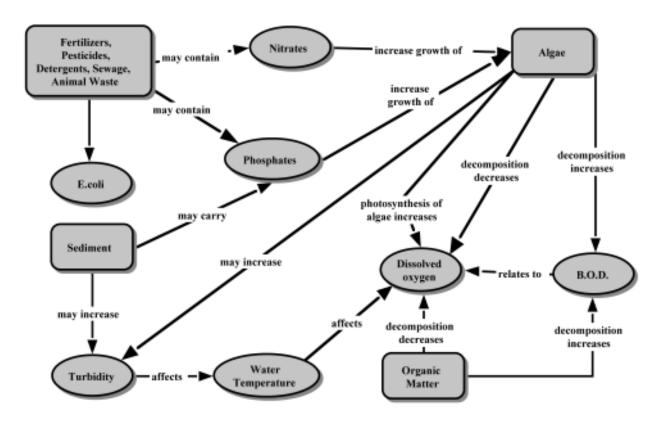
To discard chemical waste, label two separate containers with secure lids (such as a recycled margarine or milk containers). Label one "Hazardous Nitrate Waste" (HACH Nitrate Test Only) and one "Non-Hazardous Chemical Waste." Place all liquids and solids in the plastic containers along with several cups of clay cat litter. Allow the liquid to evaporate. The chemical waste is now in solid form.

You can dispose of the Hach Nitrate waste (which contains the heavy metal cadmium) by calling your local Solid Waste Management District. Your county may have Tox-Away Days which are sponsored by the Indiana Department of Environmental Management or Household Hazardous Waste Collection Days. All hazardous waste; including old paint, pesticides, cleaning agents, and Hach Nitrate waste can be taken in or picked up on these days. These collection events are designed for community members and are free.

The waste from all the other tests (including the GREEN nitrate test) is non-hazardous. Once in solid form, you can throw it away with your regular trash. If it's all in a liquid form, you may also wash it down the sink with plenty of water.

Water Monitoring Parameters are Interrelated

Aquatic chemistry is complex and is influenced by many interrelated factors. The simplified concept map below may help in understanding these relationships in an aquatic environment. The rectangles represent watershed inputs into a river or stream, while the circles represent chemical parameters we measure to determine water quality.



ppm vs mg/L

What does part per million mean? I'll explain with an example: 12 ppm of dissolved oxygen means that there are 12 molecules of oxygen in one million molecules of water. The following examples are listed on the "Water on the Web" (http://wow.nrri.umn.edu/wow/under/units.html) to provide further understanding of these units of concentration. One part-per-million is equal to:

- one car in bumper-to-bumper traffic from Cleveland to San Francisco one inch in 16 miles
- one minute in two years
 one ounce in 32 tons
 one cent in \$10,000

So, how can it be that milligram per liter (mg/L) is the same as parts per million (ppm)? Well, a milligram per liter of water is equivalent to 1 ppm (part per million) because a liter of water weighs 1000 grams and a milligram is 1 one thousandth of a gram.

This is true for freshwater since the density of freshwater is 1 g/mL ($1 \text{ g/mL} = 10^{-3} \text{ g/}10^3 \text{ mL} = 10^{-6}$, or 1 ppm), but it does not hold for salt water because density increases with salinity.

The units mg/L and ppm are equal in fresh water. They are used interchangeably throughout this chapter!

Advanced Chemical Testing Instructions*

Introduction

As explained on the first page of the Chemical Testing Instructions (page 29), this section provides information for completing the eight chemical tests using more advanced methods. Information for each test is provided in the same format: background/introduction to the test, problems & causes, checklist of equipment, instructions for use of the Hach test kits, typical ranges of results, Indiana state standards (if applicable), and Q-charts/ Q-tables for use in the Advanced Chemical Monitoring Data Sheet. See page 70 for more information about Q-values, page 72 for the Chemical Monitoring Worksheet, and page 75 for the Advanced Chemical Monitoring Data Sheet.

Typical Ranges

After each set of test instructions, you will find figures representing the likely ranges into which your chemical test results may fall. These ranges were created by determining the level at two standard deviations around average concentrations from the first 50 streams listed in the Indiana Department of Environmental Management (IDEM) 1991 monitoring records. Each range statistically represents values found on roughly two-thirds of the Indiana streams tested. In addition, the Indiana state standards for stream water quality are included for each applicable parameter. See Chapter 6, page 112, for a list of water quality standards as specified by the Indiana Administrative Code (327 IAC 2).

Times and Locations for Completing Tests

The table below provides estimated times for performing each of the tests and whether they must be completed on-site or off-site. If samples are taken off-site, they must be kept on ice or refrigerated until testing is completed (except BOD). All tests should be completed as soon as feasible to obtain the best possible results.

Chemical Test	Time to Complete	Location
Dissolved Oxygen	10-20 minutes	On-site
E . coli	5 minutes to prep / 48 hrs to incubate / 5-10 min to count	On-site/Off-site
рН	5 minutes to calibrate / 5 minutes to test	On-site
Biochemical Oxygen Demand (BOD)	5 days to incubate / 10-20 minutes	Off-site
Water Temperature Change (1 mile)	< 5 min at each location	On-site
Total Phosphates	45 minutes - 1 hour	On-site/Off-site
Orthophosphate	5-10 minutes	On-site/Off-site
Nitrates	15-20 minutes	On-site/Off-site
Turbidity	5 minutes	On-site

^{*}Information and Instructions for the Advanced Chemical Testing Section were modified with permission from the Hach Co., Earth Force-GREEN, the LaMotte Company, and the Student Watershed Research Project/Saturday Academy of Oregon.

Dissolved Oxygen

Oxygen is as important to life in water as it is to life on land. Most aquatic plants and animals require oxygen for survival, and the availability of oxygen affects their growth and development. The amount of oxygen found in water is called the dissolved oxygen (DO) concentration. Oxygen dissolves readily into the water from the atmosphere until the water is saturated. Aquatic plants, algae, and phytoplankton also produce oxygen as a by-product of photosynthesis.

DO is an important measure of stream health. Presence of oxygen in water is a positive sign, while absence of oxygen from water often indicates water pollution. Aquatic organisms require different levels of DO. Dissolved oxygen levels below 3ppm are stressful to most aquatic organisms. DO levels below 2 or 1ppm will not support fish. Levels of 5 to 6ppm are usually required for healthy growth and activity of aquatic life.

Some of the factors affecting DO are:

- Temperature (water can't hold as much dissolved oxygen at higher temperatures)
- Altitude/atmospheric pressure
- Turbulence
- Plant growth/photosynthesis
- Amount of decaying organic material

% Saturation

Two pieces of information are needed to interpret dissolved oxygen levels – the DO concentration (in ppm or mg/L) and the water temperature. From these two values, the percent saturation can be determined. Percent saturation is the level of DO in the water compared to the total amount of DO that the water has the ability to hold at a given temperature. The table on page 47 shows the mg/L of DO that represents 100% saturation at each given temperature.

Cold water can hold more dissolved oxygen than warm water. For example, water at 26°C is 100% saturated with 8ppm dissolved oxygen.

However, water at 8°C can hold up to 12ppm DO before it is 100% saturated. Thus, daily and seasonal temperature changes, as well as changes caused by thermal pollution, greatly impact oxygen levels and aquatic life in streams and rivers.

Supersaturation

High levels of bacteria or large amounts of rotting organic material can consume oxygen very rapidly and cause the percent saturation to decrease. Conversely, water may become **supersaturated** for short periods of time, holding more than 100% of the oxygen it would hold under normal conditions. Supersaturation is often caused by high levels of photosynthesis in streams overloaded with aquatic plants and algae. Supersaturation may also occur at the base of dams due to increased pressure. Supersaturation can be harmful to aquatic organisms, causing gas bubble disease, a condition similar to "the bends", which scuba divers may get if they surface too fast.

Problem

Lack of sufficient dissolved oxygen required by most aquatic organisms to breathe. Lack of oxygen increases the toxicity of other chemicals (e.g. hydrogen sulfide and ammonia).

Causes

- Rapid decomposition of organic materials, including dead algae, shoreline vegetation, manure or wastewater decreases oxygen.
- High ammonia concentrations in the stream use up oxygen in the process of oxidizing ammonia (NH₄⁺) to nitrate (NO₃⁻) through nitrification.
- Less oxygen can dissolve in water at higher temperatures.
- Lack of turbulence or mixing to expose water to atmospheric oxygen results in low dissolved oxygen concentrations.

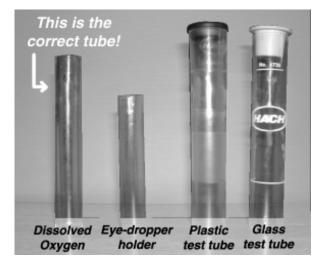
Dissolved Oxygen Instructions

These instructions are for use with the HACH Co. Dissolved Oxygen (DO) Test Kit, Cat. No. 1469-00, Model OX-2P, for 60 mL sample.

CHECKLIST

- □ DO glass collection bottle and glass stopper
 □ 23 ml square mixing bottle
 □ Plastic measuring tube (5.83ml)
 □ DO Reagent 1 powder pillows (manganous sulfate)
 □ DO Reagent 2 powder pillows (lithium hydroxide)
 □ DO Reagent 3 powder pillows (sulfamic acid)
 □ Sodium Thiosulfate Solution dropper bottle
 □ Waste container
 □ Material Safety Data Sheets
 □ Hoosier Riverwatch Manual
 □ Advanced Chemical Data Sheet and Worksheet
- 1. After rinsing thoroughly with distilled water and sample water, lower the DO bottle (or other clean collection bottle) in an upside-down position to a point well below the water's surface (3-4 inches). Turn the bottle upright to an angle tilting upstream. Allow water to flow into the bottle for 2 minutes until the bottle is full and no air bubbles are present. While the bottle is underwater, place stopper in the top. Remove the bottle from the stream with the stopper in place. Do not pour off the excess water around the rim of the stopper. (Note: If pouring your sample from another bottle into the DO bottle, be careful not to agitate or splash the water into the bottle.)
- 2. Add Dissolved Oxygen 1 Reagent and Dissolved Oxygen 2 Reagent powder pillows to the DO bottle (the order does not matter). Stopper the bottle, being very careful not to introduce air bubbles. (Note: Allow the excess water to spill over into a waste container. If you get an air bubble, start over with step one.) With your thumb firmly holding the stopper in place, grip the bottle and shake vigorously until the contents are evenly mixed. A flocculent (floc) will form. If oxygen is present in the sample, the floc will appear brownish-orange in color. A small amount of powdered reagent may remain, but will not affect the test results.

- 3. Allow the sample to stand until the floc has settled below the DO bottle's white line. The upper half of the sample will be clear. After it has settled, shake the bottle again to remix contents and allow it to resettle below the white line again. (Note: The floc will not settle in samples with high concentrations of chloride. Allow a maximum of five minutes for the floc to settle, if no progress is made, continue with the next step.)
- **4.** Add the contents of Dissolved Oxygen 3 Reagent powder pillow (*located in the white tub*). Carefully replace the stopper and shake the bottle to mix. The floc will dissolve, creating a yellowish-amber color if DO is present. (*Note: Small rust-colored flakes may remain, but will not affect the test results.*)
- 5. Fill the sturdy, plastic 5.83 mL measuring tube (1 cm width x 8.5 cm length) to its top with the prepared sample, then pour into the square mixing bottle. (Note: Do not discard the fluid in the DO bottle until you have successfully completed the rest of this test.)



6. Using the dropper located within the brown bottle marked Sodium Thiosulfate Standard Solution, add this solution drop by drop to the prepared sample in the mixing bottle. Count each drop as it is added and gently swirl to mix the solution until it becomes colorless. Once the prepared sample is clear, add one more drop to ensure a complete color change. If there is no change in color, do not count this last drop. (Note: Hold the dropper vertically above the mixing bottle's mouth

when adding drops to ensure the proper volume of solution. Do not place the dropper inside the mouth of the square bottle as you may contaminate the dropper. Important:, rinse any surface, including your hands, that has contacted the above chemical as it may "eat" holes in your clothing and/or irritate your skin.)

- 7. Each drop added to bring about the color change in Step 6 equals the presence of 1.0 mg/L of dissolved oxygen. (Note: If the result of Step 6 is 4 mg/L or less, follow the Dissolved Oxygen Low-Range 0.2 4.0 mg/L instructions provided on the next page.)
- 8. Use the graph in Figure 12 (on the next page), to calculate percent saturation. By running a straight edge from the appropriate water temperature reading to Dissolved Oxygen in mg/L, you will be able to determine percent saturation along the angled (middle) scale. If you took your water temperature in Fahrenheit, look below for a Fahrenheit to Celsius conversion, or on page 57 for a temperature conversion diagram.

$$C = (F - 32.0)/1.80$$

9. Record Dissolved Oxygen to the nearest 1.0 mg/L, and record the Percent Saturation.

Example:

Dissolved oxygen = 8 mg/L Water temperature = 16 °C Look on chart = 80% Saturation

Dissolved Oxygen Low-range (0.2-4 mg/L)

- 1. Use the prepared sample left from Step 5 of the High-range test. Pour off the contents of the DO bottle until the level reaches the white line (30 mL mark) on the bottle.
- 2. Add Sodium Thiosulfate Standard Solution one drop at a time to the DO bottle. Count each drop as it is added and gently swirl to mix the solution until it becomes colorless. Once the prepared sample is clear, add one more drop to ensure a complete color change. If there is no change in color, do not count this last drop.
- 3. Multiply the number of drops used by 0.2 to obtain the mg/L Dissolved Oxygen.

Example:

drops used x 0.2 = mg/L Dissolved Oxygen 15 drops x 0.2 = 3 mg/L Dissolved Oxygen

4. Record DO in mg/L and Percent Saturation.



Typical range for DO = 5.4 to 14.8 mg/L

Indiana Average = 9.2 mg/L

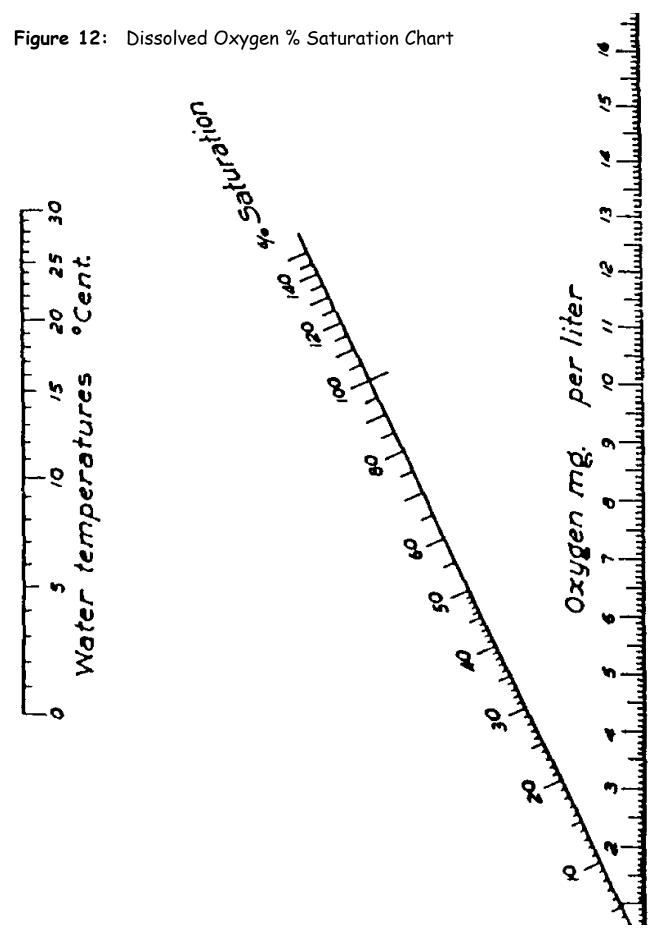
State Water Quality Standard: Avg > 5mg/L, not < 4mg/L

Percent Saturation is the % of milligrams of oxygen gas dissolved in one liter of water at a given temperature **compared with the maximum** milligrams of oxygen gas that can dissolve in one liter of water at the same temperature and pressure.

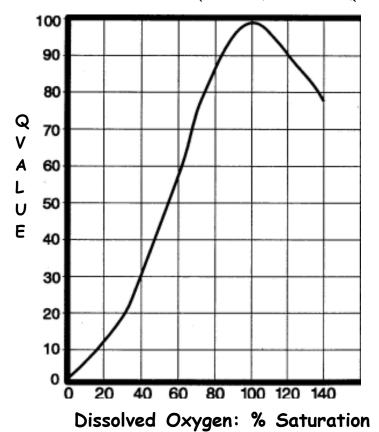
The table on page 47 tells you how much dissolved oxygen (mg/L) your water sample would need to be 100% saturated at a given temperature.

For example: If your stream temperature is 22 $^{\circ}C$, then it would be 100% saturated with dissolved oxygen at 8.90 mg/L.

Check your result obtained from the graph in Figure 9 against the table values.



Dissolved Oxygen Q-Values (For more information about Q-values, see page 70.)



DO (% Saturation)	Q-Value
0	0
10	8
20	13
30	20
40	30
50	43
60	56
70	77
80	88
85	92
90	95
95	97.5
100	99
105	98
110	95
120	90
130	85
140	78
>140	50

Dissolved Oxygen Concentration (100 % Saturated)*

TEMP 0	DISSOLVED	TEMP 0	DISSOLVED	TEMP 0	DISSOLVED
TEMPC	OXYGEN mg/L	TEMPC	OXYGEN mg/L	TEMPC	OXYGEN mg/L
1	14.60	16	10.07	31	7.41
2	14.19	17	9.85	32	7.28
3	13.81	18	9.65	33	7.16
4	13.44	19	9.45	34	7.05
5	13.09	20	9.26	35	6.93
6	12.75	21	9.07	36	6.82
7	12.43	22	8.90	37	6.71
8	12.12	23	8.72	38	6.61
9	11.83	24	8.56	39	6.51
10	11.55	25	8.24	40	6.41
11	11.27	26	8.09	41	6.31
12	11.01	27	7.95	42	6.22
13	10.76	28	7.81	43	6.13
14	10.52	29	7.67	44	6.04
15	10.29	30	7.54	45	5.95
					*at sea leve

E. coli

Fecal coliform bacteria are found in the feces of warm-blooded animals, including humans, livestock, and waterfowl. These bacteria are naturally present in the digestive tracts of animals, but are rare or absent in unpolluted waters. Fecal coliform bacteria typically enter water via combined sewer overflows (CSOs), poor septic systems, and runoff from agricultural feedlots. The bacteria can enter the body through the mouth, nose, eyes, ears, or cuts in the skin.

E. coli is a specific species of fecal coliform bacteria used in Indiana's state water quality standards. Forty-one percent (8,660 miles) of Indiana streams do not support primary contact recreation due to high E. coli bacteria levels. (Source: IDEM Integrated Water Quality Monitoring and Assessment Report, 2002)

Bacteria & Human Health

Some strains of E. coli can lead to illness in humans. While not all strains of E. coli are pathogenic themselves, they occur with other intestinal tract pathogens that may be dangerous to human health. We test for the presence of E.coli as an indicator of fecal contamination.

The US EPA has determined that *E*. coli bacteria counts above 235 colonies per 100 mL indicate that more than 8 people out of 1,000 who come into contact with the water may become sick. But it is important to remember that as *E*. coli counts go up, it is the <u>chance</u> that someone will get sick that goes up - there are many other things that determine if a person will become sick:

- how long someone is in contact with the water
- if water comes into contact with a person's eyes or mouth
- if the person has skin abrasions or wounds
- the age and health of the person, as that can determine a person's susceptibility to illness

(Source: USGS Chattahoochee BacteriALERT - http://ga2.er.usgs.gov:80/bacteria/helpwithtables.cfm)

Problem

High levels of E.coli indicate fecal contamination and the potential presence of pathogens that could cause human illness.

Causes

- Human waste from improperly functioning septic systems, wastewater treatment systems, or combined sewer overflows.
- Pet waste, wildlife (including waterfowl).
- Livestock or manure runoff from fields.

CHECKLIST

- Pre-treated petri dishes; only available through Micrology Laboratories
- Sterile pipettes, Whirl-pac bag or other sterile container (if plating is completed offsite)
- ☐ Bottle(s) of Coliscan Easygel
- Permanent marker
- □ Tape
- □ Rubber Gloves
- Ice and cooler (if plating is completed offsite)
- Bleach and water-tight bag for disposal
- Material Safety Datasheets
- ☐ Hoosier Riverwatch Manual
- Advanced Chemical Data Sheet and Worksheet

Do not rinse these materials before or after use! Follow instructions provided!

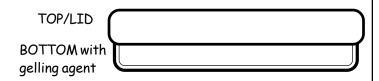
E. Coli Instructions

The following instructions are adapted from those provided by Micrology Laboratories, Inc. for use with its patented Coliscan Easygel method. For details on use and interpretation of results, please refer to the manufacturer's instructions. Be sure to request a copy of the color identification photo examples when ordering! Contact them at www.micrologylabs.com or 1-888-EASYGEL.

Easygel E. Coli Instructions

- 1. Before you begin, label the top of the petri dish with a permanent marker. Include the date, time, location, and volume (mL) of sample water used. Also, remove Coliscan Easygel bottle from freezer and allow to defrost.
- 2. Wearing gloves and using only sterile equipment, obtain a sample for testing in one of two ways. Either collect your water sample in a sterile container (e.g. Whirl-pak Bag) and transport the water to an appropriate test site, or take a measured sample directly from the source using a sterile pipette and immediately place it into the bottle of Coliscan Easygel. In either case, obtain the sample slightly below the surface. (Note: Water samples kept longer than 10 minutes prior to plating should be kept in a cooler on ice or in a refrigerator.)
- 3. Transfer a measured amount of water from the source into the bottle of Coliscan Easygel. (Note: For safety purposes and easier identification, the amount of sample used will vary according to the suspected conditions of the water you are testing. If you suspect a high fecal coliform count due to contamination from direct sewage, transfer only 0.5 1 ml of sample. Typically, however, 3-5 ml is appropriate.)

Once the sample is transferred, swirl the bottle to distribute the Easygel and then pour the mixture into the bottom half of a Micrology Labs pre-treated petri dish. (Note: If you hold the petri dish up to a light, you can see the gelling agent.) Being careful not to splash over the side or onto the lid, gently swirl and rock the filled dish until the mixture is evenly distributed across the bottom of the dish.



4. While its contents are still in liquid form, place the dish right-side-up directly onto a level location out of direct sunlight. Solidification will occur in approximately 45 minutes.

- **5.** Turn the petri dish upside down (to reduce condensation) and incubate at 35° C (95° F) for 24 hours or at room temperature for 48 hours.
- **6.** After the appropriate incubation period, inspect the dish. Count all of the purple/violet colonies in the dish and record the results in terms of *E*. coli per 100 mL of water. Do not count pinpoint colonies < 1mm in size, and disregard any pink, light blue, blue-green, or white colonies, as these indicate other types of coliforms.

To report the total number of *E*.coli per 100ml, first divide 100 by the number of mL you used in your sample, then multiply that figure by the # of colonies you counted in your petri dish.

Example: You used 3 mL of stream water & you counted 4 purple colonies in your dish.

First divide 100 by 3 = 33.3. Then multiply $33.3 \times 4 =$

133.2 colonies/100 mL

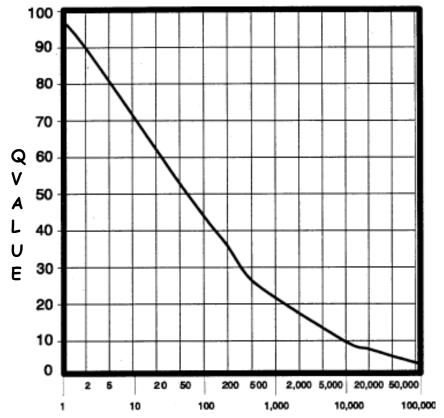
- 7. To prepare your sample bottle and petri dish for disposal in normal trash, place 5 mL (about 1 teaspoon) of 10% bleach solution onto the surface of the medium. Allow to sit for at least 5 minutes. Place in a watertight plastic bag and discard in trash.
- * Expiration: Coliscan Easygel bottles (not petri dishes) need to be stored in a freezer. The Easygel medium is good for 1 year.

Typical range for *E.* coli = 133 to 1,157 colonies/100 mL

Indiana Average = 645 colonies/100mL

State Water Quality Standard: <235 colonies / 100 mL for total body contact recreation

E. coli Q-Values (For more information about Q-values, see page 70.)



E.Coli	Q-Value
(colonies/100mL)	Q-value
0-1	98
2	89
5	80
10	71
20	63
50	53
100	45
200	37
500	27
1,000	22
2,000	18
5,000	13
10,000	10
20,000	8
50,000	5
100,000	3
>100,000	2

E-coli: colonies/100 mL

pН

The pH test is one of the most common analyses in water testing. Water (H₂O) contains both hydrogen ions (H⁺) and hydroxide ions (OH⁻). The relative concentrations of these ions determine whether a solution is acidic or basic.

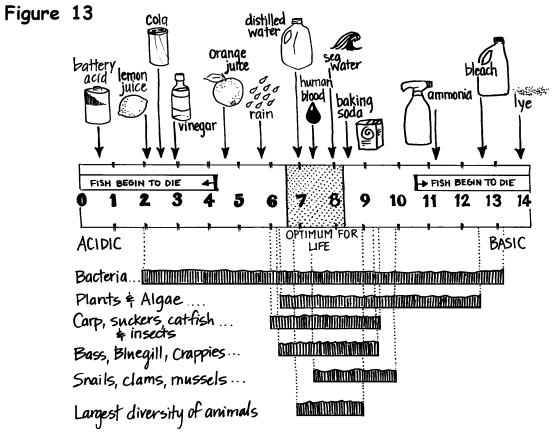
The activity of the hydrogen ions is expressed in pH units (pH = power of Hydrogen). The concentration of H⁺ ions is used to estimate pH. The pH scale ranges from 0 (most acidic) to 14 (most basic), with 7 being neutral. If the solution has more H⁺ ions than OH⁻ ions, it is acidic and has a pH less than 7. If the solution contains more OH- ions than H+ ions, it is basic with a pH greater than 7. It is important to remember that pH is measured on a logarithmic scale; it is reported as the negative log of the hydrogen ion concentration (-log [H⁺]). A change of 1 pH unit means a ten-fold change in the ion concentrations. For this reason, pH units are not normally averaged; however, to simplify calculations, Riverwatch allows volunteers to average pH.

The pH level is an important measure of water quality because aquatic organisms are sensitive to pH, especially during reproduction. Adult organisms may survive, but young will not be produced. A pH range of 6.5 to 8.2 is optimal for most organisms (see Figure 13 and page 114).

Many natural processes affect pH. Waterbodies with higher temperatures have slightly lower pH values. Also, algae blooms remove carbon dioxide (CO₂) from the water during photosynthesis, which may raise pH to 9 or more.

Runoff from abandoned mine lands can produce acid main drainage which lowers pH. Lower pH values increase the solubility of some heavy metals, such as copper and aluminum, allowing them to dissolve into the water and harm aquatic organisms.

Most natural waters have pH values of 5.0 - 8.5. Freshly fallen rainwater has a pH of 5.5 - 6.0 due to the presence of CO₂ in the atmosphere, but air pollution due to automobiles and coal-burning power plants creates acid rain which is even more acidic. Alkaline soils and minerals (limestone) can buffer the effects of acid rain and raise pH to 8.0 - 8.5.



pH Instructions

These instructions are for use with the HACH Co.'s portable pH pen, Cat. No. 44350-00, Pocket Pal Tester

CHECKLIST

- □ pH pen
 □ Jewelry or eyeglass screwdriver
 □ 50 or 100ml beaker or clean baby food jar
 □ graduated cylinder or Hach square mixing bottle
 □ pH 7.0 liquid buffer solution or powder pillows
 □ Material Safety Datasheets
 □ Hoosier Riverwatch Manual
 □ Advanced Chemical Data Sheet and Worksheet
- **1.** For accurate results, always begin by calibrating the pH meter. Follow the instructions provided in the next column.
- **2.** Once calibrated, place the pH meter into the stream so that 1/3 of its length is submerged below the water's surface. Gently swirl the meter in the water during the reading.
- **3.** Turn the meter on and allow the digital reading to stabilize. Once stabilized, record the reading.
- **4.** After each use, rinse with distilled water and turn off the pH meter to lengthen the life of the batteries. (*It uses 3 4 watch-type batteries.*)
- **4.** Place a small amount of pH 7.0 buffer in the cap before replacing to keep bulb moist.

Typical range for pH = 6.6 to 8.3 Indiana Average = 7.5

State Standard = between 6 - 9

Due to the state's limestone geology, Indiana surface waters will typically have a pH that is relatively basic (> 7).

Calibration Instructions

Step 1: Prepare the Buffer Solution

Pre-mixed liquid buffer solutions can be stored for 1 year, as long as they have not been contaminated. If you are using a pre-mixed buffer solution, measure 50 mL using a graduated cylinder or the Hach square mixing bottle and pour into a clean beaker or well-cleaned baby food jar labeled "pH 7.0 buffer." Discard solution after one day's use.

If you are using the powder pillow buffer, measure 50 mL distilled water using a graduated cylinder or the Hach square mixing bottle and pour into a clean beaker or well-cleaned baby food jar labeled "pH 7.0 buffer." Add one pH 7.0 powder pillow and shake or stir to dissolve the powder completely. Discard solution after 1 day.

Step 2: Calibration of the pH pen

(Note: This procedure can be performed before you go into the field. Since the pH pen does not have automatic temperature compensation, the buffer solution should be at 25°C. Low temperatures and low conductivity will make calibration and testing of pH slower and more difficult with a pH pen.)

- 1. If the pH pen has been stored dry, soak the electrode in pH 7.0 buffer solution for 2 24 hours before calibrating. Do not turn it on yet.
- Rinse the electrode (glass probe) with distilled water using a squeeze bottle and blot dry with a soft tissue. Do not touch the electrode with your fingers.
- 3. Turn the pen on and immerse the electrode entirely in the pH buffer as shown in the photo. Gently stir the buffer solution with the probe and wait for the reading to stabilize. (This could take a minute or two. If readings are erratic, replace the batteries.)
- 4. Use a small flathead or eyeglass screwdriver to turn the screw on the back of the pen until the reading is exactly 7.0. (*In older pH pens, the screw is inside a small hole.*)
- 5. Rinse the bulb with distilled water and blot dry.

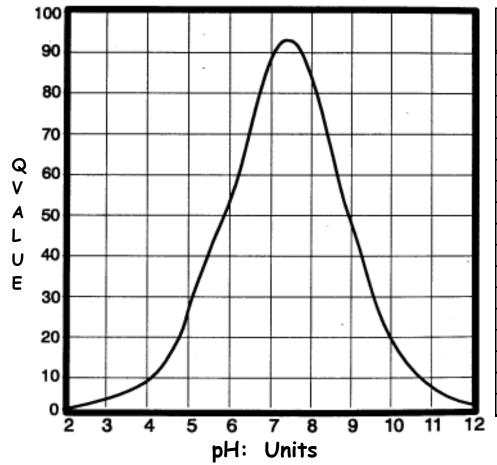
Step 3: Recheck your pH pen in the Field

Take the pH buffer solution into the field with you. If the value of the buffer solution is more than + or - 0.2 pH units from the true value, repeat the calibration procedure again.



pH Q-Values

(For more information about Q-values, see page 70.)



ıs U	O Value
рН	Q-Value
(units)	
<2	0
2	2
3	4
4	8
5	24
6	55
7	90
7.2	92
7.5	93 (max)
7.7	90
8	82
8.5	67
9	47
10	19
11	7
12	2
>12	0

Biochemical Oxygen Demand

Biochemical oxygen demand (BOD₅) is a measure of the amount of oxygen used by aerobic (oxygen-consuming) bacteria as they break down organic wastes over five days. Polluted streams, or streams with a lot of plant growth (and decay), generally have high BOD₅ levels. High levels indicate that large amounts of organic matter are present in the stream. Streams that are relatively clean and free from excessive plant growth typically have low BOD₅ levels.

In slow moving and polluted waters, much of the available dissolved oxygen (DO) is consumed by bacteria, which rob other aquatic organisms of the oxygen needed to live. Streams with higher DO levels, such as fast-moving, turbulent, coldwater streams, can process a greater quantity of organic material. Therefore, interpretation of BOD_5 levels depends upon the conditions of the stream sampled, as some streams can "handle" more waste than others. However, in general, a healthy stream has high DO levels and low BOD_5 levels – be careful not to confuse the two!

The following is a rough guide to what various BOD₅ levels indicate:

$1-2 \text{ mg/L BOD}_5$	Clean water with little organic waste
$3-5 \text{ mg/L BOD}_5$	Fairly clean with some organic waste
$6-9 \mathrm{mg/L}\mathrm{BOD}_5$	Lots of organic material and bacteria
10+ mg/L BOD ₅	Very poor water quality. Very large
	amounts of organic material in water.

Problem

High levels of organic matter - including leaves, dead fish, garbage, some industrial waste, fertilizer, pet waste, and sewage from poor functioning septic systems or combined sewer overflows - and some ions (ammonia in particular) can lead to rapid exhaustion of dissolved oxygen.

Causes

 Municipal wastewater and septic tank effluent that has not been completely treated will use up oxygen.

BOD5 Instructions

In addition to a black (light-free) bottle, use the HACH Company's Dissolved Oxygen (DO) Test Kit with Cat. No. 1469-00, Model OX-2P, for 60 mL sample.

CHECKLIST

- BOD Bottle (if available); if not, use aluminum foil around DO bottle or hydrogen peroxide bottle
- All materials required for dissolved oxygen test See list on page 44
- 1. Rinse, then lower a stoppered black (light-free) bottle below the water's surface. Allow water to flow into the bottle for approximately 2 minutes. Ensuring that no air bubbles exist, replace the stopper and remove the bottle from the water.
- **2.** Place the BOD sample in a light-free location (e.g., desk drawer) at room temperature and allow it to sit undisturbed at approximately 20 °C (68 °F) for 5 days.
- **3.** After 5 days, remove the BOD bottle and perform Steps 1 through 8 of the DO test using the water from the BOD bottle. If results are <4 mg/L, follow the Low-range DO test instructions (see pages 44-45).
- **4.** Determine the BOD level by subtracting the mg/L of the BOD sample from that of the original DO sample taken 5 days prior.

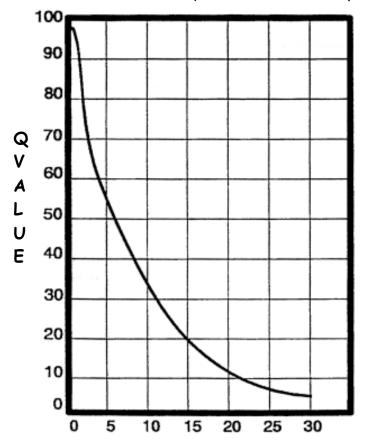
Example: 11 mg/L (original DO - day 1)
- 6 mg/L (DO 5 days later)
5 mg/L (BOD_c)

Typical range for $BOD_5 = 1.1 - 3.3 \text{ mg/L}$ Indiana Average = 2.2 mg/L

Note: If DO is not detected after 5-day period, the BOD of the sample cannot be determined. In this case, report BOD as $> DO_{day1}$ and note that no DO was detectable after 5 days.

 Eutrophication and hot weather can cause algae blooms. When bacteria decompose the dead algae, oxygen is consumed which increases BOD.

BOD5 Q-Values (For more information about Q-values, see page 70.)



DO (%Saturation)	Q-Value
0	0
10	8
20	13
30	20
40	30
50	43
60	56
70	77
80	88
85	92
90	95
95	97.5
100	99
105	98
110	95
120	90
130	85
140	78
>140	50

BOD₅: mg/L

Water Temperature Change (1 mile)

Water temperature is very important to overall water and stream quality. Temperature affects:

- 1. Dissolved Oxygen Levels Colder water can hold more dissolved oxygen than warmer water, thus colder water generally has higher macroinvertebrate diversity. Warmer water has less dissolved oxygen. Lower oxygen levels weaken fish and aquatic insects, making them more susceptible to illness and disease (See Figure 14).
- 2. Rate of Photosynthesis Photosynthesis by algae and aquatic plants increases with increased temperature. Increased plant/algal growth leads to increased death and decomposition, resulting in increased oxygen consumption (BOD₅) by bacteria.
- 3. Metabolic Rates of Aquatic Organisms Many animals require specific temperatures to survive. Water temperature controls their metabolic rates, and most organisms operate efficiently within a limited temperature range. Aquatic organisms die when temperatures are too high or too low.

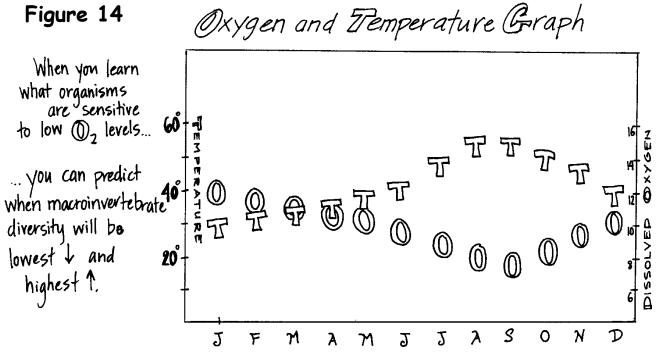
Water temperature varies naturally with changes of the seasons, the amount of rainfall, and flow rates. Thermal pollution (temperature increases) can threaten the balance of aquatic ecosystems. To determine if your river or stream is thermally polluted you must take a temperature reading at two different locations. Increased water temperature may be caused by many sources, some of which are listed below. If water temperature decreases within a mile of the sampling site, there may be a source of cold water, such as a spring, entering the stream.

Problem

Aquatic organisms have narrow optimal temperature ranges. In addition warmer water holds less dissolved oxygen.

Causes

- Loss of shading by trees in the riparian zone and the watershed.
- Runoff from roads and parking lots
- Discharges from municipal wastewater and industrial sources.



The air temperature needs to be taken while the thermometer is completely dry, so do that first! Hang the thermometer somewhere where it's not leaning against a solid object and where it's protected from direct wind and sunlight.

The thermometer will take 5 - 10 minutes to equilibrate. Record the result!

Temperature Change Instructions

- 1. Place the thermometer below the water's surface (e.g., the same depth at which other tests are performed). If possible, obtain the temperature reading in the main streamflow.
- **2.** Swirling gently, hold the thermometer in the water for approximately 2 minutes or until the reading stabilizes.
- **3.** Record your reading in Celsius. (Note: If you are using a thermometer that reads only in Fahrenheit, look at Figure 15 or use the following equation to convert to Celsius:

$$C = (F - 32.0)/1.8$$

- 4. Choose a portion of the stream with roughly the same degree of shade and velocity as in Step 1, and conduct the same test approximately 1 mile upstream as soon as possible using the same thermometer.
- **5.** Calculate the difference between the downstream and upstream results. Record the temperature change in Celsius and note if the change is positive or negative.

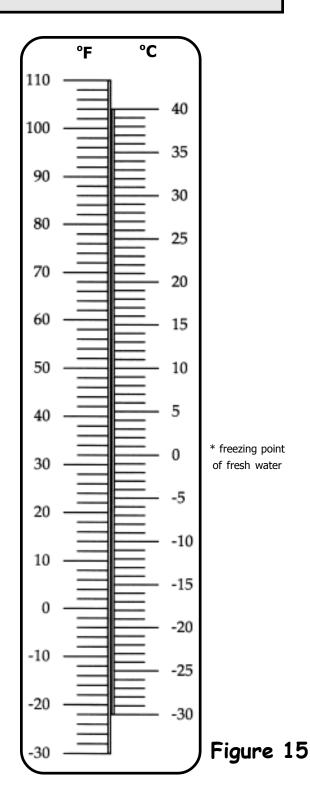
Example:

Downstream Temp (Your Site)

- Upstream 1-mile Temp
- = Temperature Change (+/-)

State Standard:

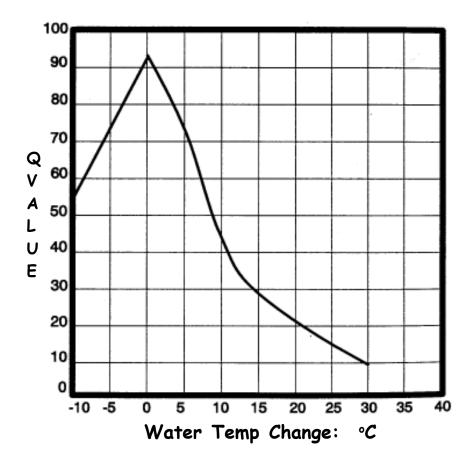
- < 5° F change downstream (approximately 2.8° C)
- < 2° F change for trout streams (approximately 1.1° C)



Temperature conversion image and air temp instructions provided by Friends of Casco Bay, ME.

Temperature Change Q-Values

(For more information about Q-values, see page 70.)



Change in Temp. (°C)	Q-Value
-10	56
-7.5	63
-5	73
-2.5	85
-1	90
0	93 (max)
1	89
2.5	85
5	72
7.5	57
10	44
12.5	36
15	28
17.5	23
20	21
22.5	18
25	15
27.5	12
30	10

Orthophosphate and Total Phosphate (PO₄)

Phosphorus is essential to plant and animal life, and its presence in the environment is natural. Problems with phosphorus as a water pollutant result not from its presence, but from the addition of excessive amounts. Aquatic ecosystems develop with very low levels of phosphorus. The addition of seemingly small amounts of phosphorus can lead to problematic algal blooms when added to aquatic systems.

Phosphorus enters surface waters in organic matter (dead plants and animals, animal waste), attached or adsorbed to soil particles, or in a number of man-made products (detergents, fertilizers, industry wastes). Phosphorus is an important nutrient in fertilizer because it increases terrestrial plant growth (vegetation). When transported into aquatic systems, phosphorus increases aquatic plant growth (e.g. algae, weeds), as well. When phosphorus levels are too high, excess plant and algal growth creates water quality problems. Plants begin to die and decompose, depleting the dissolved oxygen supply in the water - a condition called **hypoxia**, which can lead to fish kills in some cases. Phosphorus is also released from the sediments and decomposing plants back into the water, continuing the cycle. The reaction of the aquatic system to an overloading of nutrients is known as eutrophication. (See Figure 16 on the next page). Hypoxia and eutrophication, to some extent, occur within many of our lakes and streams every year, and occur on a larger scale at the mouth of the Mississippi River where there's a large "dead zone" in the Gulf of Mexico.

Orthophosphate

Phosphorus (P) occurs in nature in the form of phosphates (PO₄). Phosphate levels higher than 0.03ppm contribute to increased plant growth. Orthophosphates are one form of phosphates. Orthophosphates are dissolved in the water (mostly inorganic) and are readily available for plant uptake. Thus, the orthophosphate concentration is useful as an indicator of *current* potential for algae blooms and eutrophication.

Total Phosphate

Unlike nitrogen and other nutrients, phosphorus does not have a gaseous phase. Once it is in an aquatic system, it remains there and cycles through different forms unless physically removed. Over time some of the other forms of phosphates attached to particles in the water column and in the sediments (including organic forms) can be changed into orthophosphates, becoming available for plant growth. For this reason, it is important to test for all forms of phosphates or *total* phosphate levels.

* Results of the <u>total phosphate</u> test (*not* the orthophosphate test) are used in the Q-values, the Advanced Chemistry Data Sheet and Water Quality Index calculations on page 75.

Problem

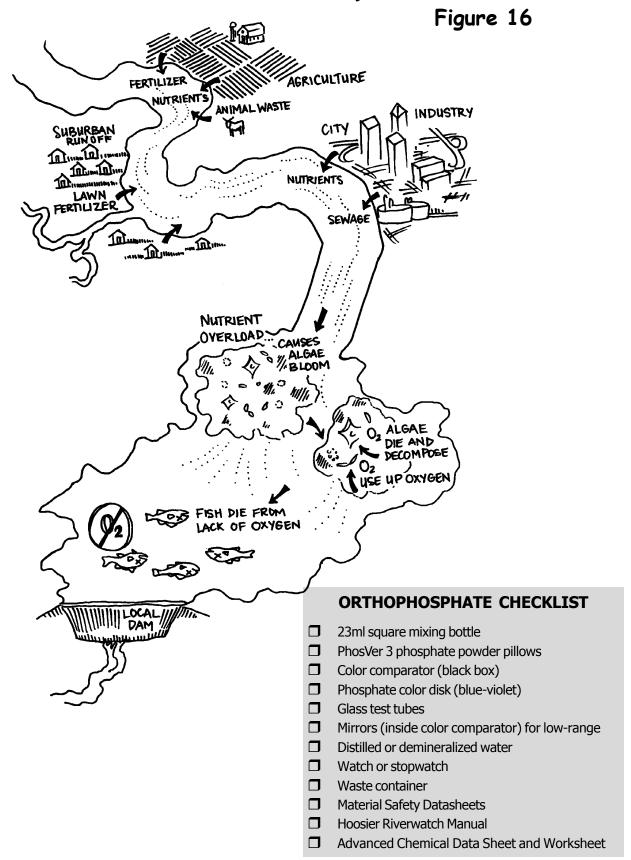
Most fresh water has naturally low phosphorus levels, and this limits algal growth. If excessive phosphates enter surface water, it can support rapid algal growth. When the algae die, their decomposition by bacteria uses up oxygen and may produce odors and algal toxins.

Causes

- Phosphorus occurs naturally in soil. Suspended sediments from soil erosion and runoff are often a significant source of phosphorus. These may enter the stream via stream bank erosion or runoff from forestry, agriculture, and urban lands. Phosphorus can desorb from soil particles and enter solution.
- Phosphorus can come from manure sources, such as treatment lagoons, overfertilized agricultural fields, or waterfowl.
- Urban sources of phosphorus may include: storm drains, parking lot and road runoff, construction sites, inadequately treated municipal wastewater and septic tank effluent, and lawn fertilizer.

EUTROPHICATION

(NUTRIENT OVERLOAD)



Orthophosphate Instructions

These instructions are for use with the HACH Orthophosphate test, for 25 mL sample, included in the Stream Survey Kit (Cat# 27120-00). They are not compatible with the Orthophosphate test (for 5 mL sample) in the HACH Surface Waters Kit (# 25598-00).

Orthophosphate Low-range test (0-1 mg/L)

- **1.** Rinse and fill the square mixing bottle to the 20-mL mark with the water to be tested.
- 2. Open one PhosVer 3 Phosphate Powder Pillow and add its contents to the bottle. Gently swirl to mix for 30 seconds. Allow at least two, but not more than ten minutes for full color development. (Note: If phosphate is present, a blue color will develop.)
- **3.** Place the mirrors onto the shelf in the color comparator. Place the Phosphate (blue-violet) color disk into the comparator. (Note: The mirrors are used only during the Low-range Orthophosphate and Total Phosphate tests.)
- **4.** Fill one of the glass test tubes to the top line with prepared sample. Place the tube on the right side of the comparator. (Note: Keep the rest of the prepared sample in the square mixing bottle until the test is complete. If the results are greater than 1mg/L, you can use the same sample for the 0-5 m/L test as explained in the shortcut.)
- **5.** Fill the other glass tube to the top line with untreated sample water and place it on the left.
- 6. Do not place caps on the tubes. Orient the comparator with the tube tops pointing to a window or light source. Rotate the disc until a color match is obtained. Divide the reading from the scale window by 50 to obtain the Orthophosphate (PO₄³⁻) in mg/L.
- ♦ SHORTCUT FOR 0-5 mg/L METHOD!

 If the result is > 1mg/L and it has been less than 10 minutes, remove mirrors from the comparator read the results again using the color comparator. Divide the reading from the scale window by 10 to obtain mg/L

 Orthophosphate.

Orthophosphate Medium-range test (0-5 mg/L)

1. Follow steps #1 and 2 of the Low-range test.

- **2.** Fill one of the <u>glass</u> tubes to the bottom line with prepared sample (approx. 5 mL). Place the tube on the right side of the comparator.
- **3.** Fill the other glass tube to the bottom line with untreated sample water and place on the left side.
- 4. <u>Do not use the mirrors</u> in the comparator. Hold the comparator up to a light source and rotate the disc until a color match is obtained. <u>Divide the reading from the scale window by 10</u> to obtain mg/L Orthophosphate (PO₄³⁻). (Note: Holding a piece of white paper 6-8 inches behind the comparator may help in viewing the color.)

Orthophosphate High-range test (0-50 mg/L)

- 1. Rinse the square mixing bottle and dropper with distilled water. Add 2.0 mL of sample by twice filling the dropper to the 1.0 mL mark.
- **2.** Add demineralized or distilled water to the 20 mL mark on the mixing bottle. Swirl to mix.
- **3.** Open one PhosVer 3 Phosphate Powder Pillow. Add the contents to the bottle. Gently swirl to mix for 30 seconds. Allow at least two minutes, but no longer than ten minutes, for color development.
- **4.** Fill one of the <u>glass</u> tubes to the bottom line with prepared sample (approx. 5 mL). Place the tube on the right side of the comparator.
- **5.** Fill the other glass tube to the bottom line with untreated sample water and place it on the left side.
- **6. Do not use the mirrors** in the comparator. Hold the comparator up to a light source and rotate the disc until a color match is obtained. Read the mg/L Orthophosphate (PO₄-3) directly on the scale.

Results of the OP test can be entered in the database as an 'extra' test. Type in the result at the bottom of the Advanced data sheet - there is no drop down menu.

There is no Q-value for Orthophosphate.

Do not enter the result on the

Advanced Chemistry Data Sheet.

There are no State Water Quality Standards for Orthophosphate.

Total Phosphate Instructions

These instructions are for use with the HACH Total Phosphate (Cat# 2250-01, Model PO-24) test, for 25 mL sample, which is included in the Stream Survey Kit (Cat# 27120-00).

- For greater accuracy and safety, it is recommended that this test be performed inside in a well-ventilated setting.
- All glassware to be used for this test should be acid washed with a dilute hydrochloric acid solution (10:1) and triple-rinsed with distilled water before each use. If acid is not available, use Isopropyl alcohol and triple rinse with distilled water. Wrap in aluminum foil to retain cleanliness. This glassware should be dedicated for the purpose of analyzing phosphorus samples.
- Orthophosphate (OP) is one component that makes up Total Phosphate (TP), thus OP < TP. These tests have three levels: low, medium, and high range. To help determine which level of the Total Phosphate test to perform, you may complete the Orthophosphate test first.
- "Digesting" (acidifying and heating) the sample coverts all other forms of dissolved and suspended inorganic & organic phosphorus to orthophosphate.

CHECKLIST

23ml square mixing bottle
Potassium persulfate powder pillows
PhosVer 3 phosphate powder pillows
Color comparator (black box)
Phosphate color disk (blue-violet)
Glass test tubes
Mirrors (inside color comparator) for low-range
Distilled or demineralized water
50 mL Erlenmeyer flask (for Total Phosphate)
5.25N sulfuric acid solution (for Total Phosphate)
5.0N sodium hydroxide (for Total Phosphate)
Hot plate, camp stove, or other heating
apparatus (for Total Phosphate only)
Tongs, oven mitt, or other device to remove
Erlenmeyer flask from heating source
Watch or stopwatch
Waste container
Material Safety Datasheets
Hoosier Riverwatch Manual
Advanced Chemical Data Sheet and Worksheet

Total Phosphate (All Levels)

- 1. Rinse with distilled water and sample water and fill the square mixing bottle to the 20 mL mark with the water to be tested. Pour the sample into a clean and rinsed 50 mL Erlenmeyer flask.
- **2.** Open one Potassium Persulfate Powder Pillow and add its contents to the flask. Gently swirl to mix.
- 3. Add 2 mL of 5.25N Sulfuric Acid Solution to the sample by twice filling the dropper to the 1 mL mark and discharging the contents into the flask. Gently swirl to mix. (*Note:* Rinse thoroughly any surfaces, including your skin, that may have contacted the acidic solution.)
- 4. Set up the boiling apparatus. (*Note:* A hot plate or camping stove is easier and more reliable than the fuel tablets provided with the kit.)
- **5.** Boil the sample for 30 minutes, occasionally adding demineralized or distilled water to keep the liquid volume near 20mL. Do not bring the volume above 20 mL. DO NOT let it boil to dryness (it will give off toxic fumes).
- **6.** Remove from heat source and allow to cool.
- **7.** Add 2 mL of 5.0N Sodium Hydroxide Solution by twice filling the dropper to the 1 mL mark and discharge the contents into the flask.
- **8.** Return sample to the square mixing bottle. Add distilled water to return its volume to 20 mL. You have now digested the sample and "turned" all the P into orthophosphate.
- 9. Using the prepared sample, follow the orthophosphate test instructions on page 61 beginning with step 2 of the Low-Range test. Your final result after completing all calculations will be mg/L Total Phosphate (PO₄) (not Orthophosphate).

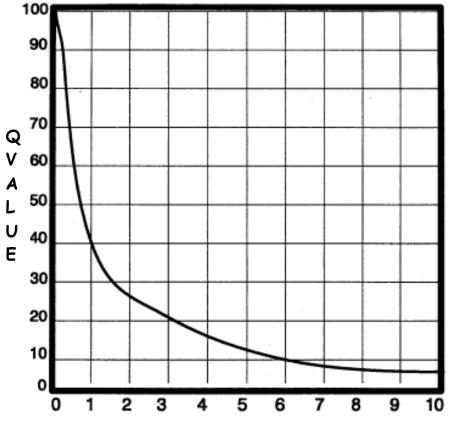
Typical range for Total Phosphate = 0.01 to 0.17 mg/L

Indiana Average = 0.09 mg/L

State Standard: < 0.04 mg/L for Lake Michigan

Total Phosphate (PO_4) Q-Values

(For more information about Q-values, see page 70.)



Total Phosphate	Q-Value
(mg/L P)	00
0	99
0.05	98
0.1	97
0.2	95
0.3	90
0.4	78
0.5	60
0.75	50
1	39
1.5	30
2	26
3	21
4	16
5	12
6	10
7	8
8	7
9	6
10	5
>10	2

Nitrate (0-1, 0-10 mg/L)

Nitrogen makes up about 80% of the air we breathe, and it is found in all living things. Nitrogen occurs in water as nitrate (NO₃), nitrite (NO₂), and ammonia (NH₃). It enters the water from human and animal waste, decomposing organic matter, and runoff of fertilizer from lawns and crops.

Nitrates are an essential nutrient for plant growth. Similar to phosphates, these are a main ingredient in fertilizers and can lead to increased aquatic plant growth and eutrophication. Unpolluted waters generally have a nitrate level below 4ppm (mg/L). Nitrate levels above 40ppm (mg/L) are considered unsafe for drinking water. (See page 59 for a more detailed discussion of eutrophication and nutrients.)

Problem

Nitrogen works with phosphorus to increase algae growth and cause eutrophication.

Causes

- Nitrogen can come from manure, such as treatment lagoons and over fertilized fields.
- Nitrogen is the most abundant nutrient in commercial fertilizers. Runoff from agriculture, golf courses, and lawns is high in nitrogen, especially if it rains soon after fertilization.
- ♦ Sewers are the #1 source in Indiana.

CHECKLIST

Plastic test tubes and stoppers NitraVer 6 Nitrate reagent powder pillows NitriVer 3 Nitrite reagent powder pillows Color comparator (black box) Nitrate color disk (pink) Distilled water Watch or stopwatch Separate waste container labeled "Hazardous" **Material Safety Datasheets** Hoosier Riverwatch Manual П Advanced Chemical Data Sheet and Worksheet **Nitrate Instructions** - For use with the HACH Low Range Nitrate Nitrogen, Cat. #14161-00, Model NI-14, for 5 mL sample. (This kit has been distributed in Riverwatch grants since 1998.) Note: Samples colder than 20°C (69°F) may react more slowly.

Nitrate Nitrogen 0-1 mg/L:

- 1. Rinse the <u>plastic</u> test tubes with distilled water and the sample to be tested. Fill one test tube to the lowest mark (the bottom of the frosted band, approx. 5 mL) with sample water.
- 2. Add the contents of the <u>NitraVer 6 Nitrate</u> powder pillow to the sample to be tested. Stopper the tube and shake vigorously for three minutes. Allow the sample to sit undisturbed for an additional 30 seconds.
- **3.** Add the contents of one <u>NitriVer 3 Nitrite</u> powder pillow to the sample. Stopper the tube and shake vigorously for 30 seconds. A <u>pink</u> color will develop if nitrate is present. Allow at least 10 minutes, but not more than 20 minutes, before completing Steps 4 through 6.
- **4.** Insert the tube of prepared sample into the right top opening of the color comparator.
- **5.** Fill a second test tube to the lowest mark with untreated sample water and place in the left side of the comparator.
- 6. Place the pink disk into the color comparator. <u>Do not use the mirrors</u>. Hold the comparator up to a light source. Rotate the disc to obtain a color match. (Note: Holding a piece of white paper 6-8 inches behind the comparator may help in viewing the color.) Read the mg/L nitrate nitrogen (N) through the scale window. <u>Multiply the reading on the scale by 4.4</u> to obtain results as mg/L nitrate (NO₃).
- 7. Place waste in Hazardous Waste container.
- ♦ SHORTCUT FOR 0-10 mg/L METHOD!

 If the concentration is > 1 mg/L and it has been less than 20 minutes, you may use your prepared sample from the low-range test to perform the 0-10 mg/L test. Use an eye dropper to measure 0.5 mL of prepared sample and add it to an empty test tube, then fill this tube to the lowest mark with distilled water. Obtain a result from the scale window and multiply by 10. Then multiply by 4.4 to obtain mg/L nitrate NO₃.

Nitrate Nitrogen 0-10 mg/L:

- 1. Rinse the <u>plastic</u> test tubes and a plastic dropper with sample water. Fill the dropper to the 0.5 mL mark with sample and discharge into one rinsed test tube.
- 2. Fill the tube containing 0.5 mL of sample to the bottom of the frosted band with distilled water.
- 3. Add the contents of one <u>NitraVer 6 Nitrate</u> powder pillow to the sample to be tested. Stopper the tube and shake vigorously for three minutes. Allow the sample to sit undisturbed for an additional 30 seconds.
- **4.** Add the contents of one <u>NitriVer 3 Nitrite</u> powder pillow to the sample. Stopper the tube and shake vigorously for 30 seconds. A <u>pink</u> color will develop if nitrate is present. Allow at least 10 minutes, but no more than 20 minutes, before completing Steps 5 through 7.
- **5.** Insert the tube containing the prepared sample into the right opening of the color comparator.
- **6.** Fill a second test tube to the lowest mark with untreated sample water and place in the left side of the comparator.
- 7. Place the pink disk into the color comparator.

 <u>Do not use the mirrors.</u> Hold the comparator up to a light source. Rotate the disc to obtain a color match. (*Note: Holding a piece of white paper 6-8 inches behind the comparator may help in viewing the color.*) Multiply that reading by 10 to obtain the mg/L nitrate nitrogen (N) present in the sample. Then multiply by 4.4 to obtain mg/L nitrate (NO₂).
- 8. Place waste in Hazardous Waste container.

Typical range for NITRATE (NO_3)= 4.18 to 13.86 mg/L

Indiana Average = 9.02 mg/L

State Standards: < 44 mg/L

Nitrate NO₃ (the value after the result is multiplied by 4.4) is used in the Q-Value chart and the Water Quality Index data sheet.

Nirate (O-50 mg/L)

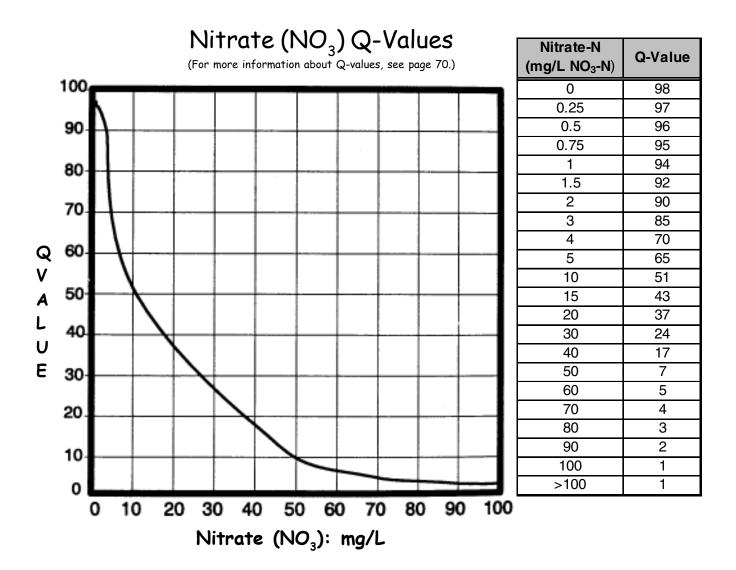
Instructions – These instructions are for use with the HACH Company's Nitrate Test Kit 0-50 mg/L, Cat.#1468-03. (This test was distributed in the Surface Waters kit Cat.#25598-00 in grants prior to 1998.)

CHECKLIST

- ☐ Plastic test tubes (viewing tubes) and stoppers
 ☐ NitraVer 5 nitrate reagent powder pillows
 ☐ Color comparator (black box)
 ☐ Nitrate color disk (amber)
 ☐ Watch or stopwatch
 ☐ Separate waste container labeled "Hazardous"
 ☐ Material Safety Datasheets
 ☐ Hoosier Riverwatch Manual
- 1. Rinse one plastic test tube with the water to be tested. Fill the tube to the 5 mL mark (bottom of the frosted band).

☐ Advanced Chemical Worksheet and Data Sheet

- 2. Use the clippers to open one <u>Nitraver 5</u> Nitrate Powder Pillow and add its contents to the tube. Stopper the tube and shake vigorously for exactly 1 minute.
- **3.** Allow the prepared sample to sit undisturbed for 1 minute. An <u>amber color</u> will develop if nitrate is present.
- **4.** Place the tube of the prepared sample in the right opening of the comparator.
- **5.** Fill the other viewing tube to the 5 ml mark with sample water and place it in the left opening of the comparator.
- 6. Place the amber disc into the color comparator. Hold the comparator up to a light source (e.g., sky or window) and view the tubes through the windows near the center of the instrument. Rotate the disc to obtain a color match. (Holding a piece of white paper 6-8 inches behind the comparator may help in viewing the color.)
- 7. Read the mg/L nitrate nitrogen (N) through the scale window. For the Water Quality Index, nitrate (NO₃) is needed. Multiply by 4.4 to obtain mg/L nitrate (NO₃).
- 8. Place waste in Hazardous Waste container.



Turbidity/Transparency

Turbidity is the relative clarity of the water and is measured by shining a light through the water column. Turbid water is more cloudy, and is caused by suspended matter including clay, silt, organic and inorganic matter, and algae. These materials scatter and absorb light, rather than allowing it to shine through the water column in a straight line. Turbidity should not be confused with color, since darkly colored water (like tea) can still be clear and not turbid.

Turbid water may be the result of soil erosion, urban runoff, algal blooms, and bottom sediment disturbances caused by boat traffic or abundant bottom feeding fish.

If a stream is very turbid, light will not reach through the water column and many reactions, especially photosynthesis, will be limited. When water is turbid, the floating particles absorb heat from the sun, raising water temperature and thus lowering dissolved oxygen levels. The particles can also kill fish and aquatic invertebrates by clogging their gills and smothering their habitat.

Transparency measures the scattering of light and is observed by the depth at which we can see an object in the water column. We measure the transparency of our water sample, and use a predetermined relationship to convert our transparency results (cm) to units of turbidity (NTUs).

Problem

The water looks "dirty." Photosynthesis is limited because organisms in the water column receive no light. Temperature is increased due to light absorption.

Causes

- Soil erosion and runoff from agricultural fields, lawns, parking lots, construction sites, or the stream bank itself.
- Algae and organic matter also contribute to turbidity.

Transparency Tube Instructions

Turbidity is assessed with a very accurate but expensive electronic turbidimeter. Transparency can be assessed with many types of equipment, including a homemade Secchi disk or transparency tube. See Appendix A for information about purchasing or making your own transparency tube.

CHECKLIST Transparency Tube Bucket Hoosier Riverwatch Manual Advanced Chemical Data Sheet and Worksheet

For use with a Transparency Tube:

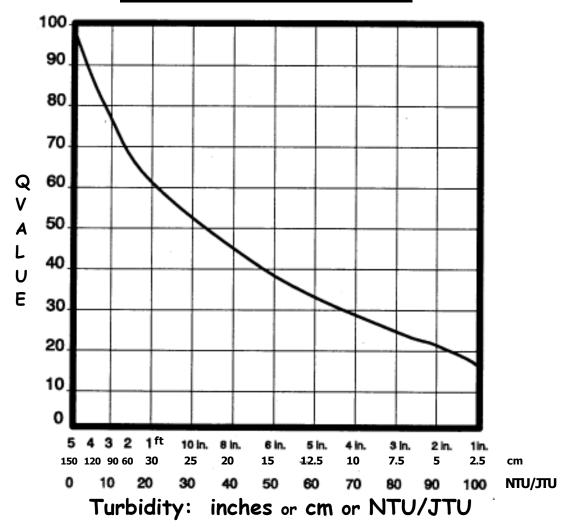
- 1. Rinse sample container with sample water. Collect sample water in a bucket or other container from which you can pour the water into a calibrated transparency tube. (Note: Avoid stirring bottom sediments when sampling at midstream.)
- **2.** Avoid direct sunlight by turning your back to the sun. Swirl the water in your bucket to mix and slowly pour sample water into the tube until the symbol is not visible.
- 3. While looking vertically down into the tube, release water until the point at which you can barely see the "X" on the bottom of the tube, and record the result in centimeters or inches. (Note: Do not wear sunglasses while taking this measurement.)
- **4.** Repeat the above steps to verify the result. (Note: Allowing one or two people to repeat the test may help obtain a more accurate result.)
- 5. Convert the tube reading from inches or centimeters to Nephelometer Turbidity Units (NTUs) using the Q-Value chart on the next page. If the symbol is still visible when your tube in full, indicate this on your data sheet:
 - > 60 cm; which is equal to < 15 NTUs
- 6 Clean your transparency tube see Appendix A-1.

Typical range for TURBIDITY = 4.5 - 17.5 NTU
Indiana Average = 11 NTU

Turbidity Q-Values

(For more information about Q-values, see page 70.)

Turbidity (NTU)	Transparency (cm)	Q-Value
0	150	97
5	120	84
10	90	76
<15 (turb tube)	>60 (turb tube)	70
15	60	68
20	30	62
25	27.5	57
30	25	53
35	22.5	48
40	20	45
50	15	39
60	12.5	34
70	10	28
80	7.5	25
90	5	22
100	2.5	17
>100	<2.5	5



OTHER RESULTS

Other water chemistry results could include tests such as ammonia nitrogen, total solids, chlorine, conductivity, alkalinity, hardness, heavy metals, or pesticides. Any chemical test results you obtain should be recorded on the data sheet.

AMMONIA NITROGEN

Although this test is not included in the water quality rating, it is included in the HACH Stream Survey test kit, and can be an indicator of pollution. Ammonia nitrogen can enter water systems from several sources including industry, sewage, and fertilizers. It is a natural degradation product of excretion and decay of dead organisms. Ammonia is a form of nitrogen that plants use for growth, but at high concentrations it is poisonous to animals, including humans. The toxicity of ammonia increases as pH increases.

- 1. Rinse test tubes with sample water and fill to the 5mL mark (bottom of the frosted band).
- **2.** Add the contents of one Ammonia Salicylate Powder Pillow to one tube. Cap and shake until the powder is dissolved. Wait 3 min.
- 3. Add the contents of one Ammonia Cyanurate Powder pillow to the prepared sample. Shake until the powder is dissolved. Wait 15 minutes for the color to develop.
- 4. Insert the tube containing the prepared sample into the right opening of the color comparator. Place the second test tube with untreated sample water in the left opening.
- **5.** Hold the comparator up to a light source. Rotate disk until a color match is obtained, then read the result in mg/L ammonia nitrogen.

TOTAL SOLIDS

Total Solids was one of the original tests included in the Water Quality Index (WQI) developed by the National Sanitation Foundation, and was included on the Hoosier Riverwatch Chemical Data Sheet from 1996-2000. This test measures the amount of dissolved and suspended solids in the water. Total Solids are measured using a very sensitive scale and a drying oven.

Most volunteer groups do not have access to the more expensive equipment required to perform this test, thus it was moved to the "optional" category.

The following instructions are adapted from the second edition of the *Field Manual for Global Low-Cost Water Quality Monitoring* (Stapp and Mitchell, 1997).

- 1. Fill a container with 100 mL of sample water. Remove any large floating particles or submerged masses from the sample.
- **2.** Take the sample to a location that has both a sensitive scale (reads to 0.0001g) and a heat source (oven) for evaporating water.
- 3. Clean and completely dry a 300 mL beaker. Weigh it and record the result. (Note: Drying the beaker in a 103°C oven for one hour is recommended. In addition, use tongs or gloves when handling the beaker to limit the transfer of body moisture or oils.)
- **4.** Pour the 100 mL sample into the 300 mL beaker. Rinse the original container with a small amount of distilled water to ensure that the entire sample is removed. Pour the rinse into the 300 ml beaker.
- 5. Place the 300 mL beaker containing the sample water onto the heat source. (*Note:* Drying the beaker in a 103°C oven overnight is recommended.) Without boiling, evaporate all of the liquids, being careful not to damage the glass beaker. Use tongs or gloves to remove the beaker from the heat source and allow it to cool. (*Note: Be very careful where you place the beaker. Do not contaminate it.*)
- **6.** Determine the weight of the total solids by subtracting the original dry weight of the beaker from that of the beaker containing the residue after evaporation.
- 7. Use the formula below to calculate total solids:

weight of residue (g) \times 1000 mg \times 1000 mL = mg/L volume of sample (mL) \times 1 g \times 1 L

Example: weight of beaker + residue 50.0250 g weight of beaker - 50.0000 g (weight of residue) 0.0250 g

.0250 g x 1,000 mg x 1,000 mL = **250 mg/L** 100 mL 1 g 1 L

Advanced Chemical Monitoring Worksheet & Data Sheet

Why use the chemical monitoring worksheet?

The chemical monitoring worksheet (page 72) can be taken into the field to record the results of multiple samples. Hoosier Riverwatch recommends that volunteers take multiple samples to assure higher quality stream monitoring results. Up to <u>three samples</u> can be recorded on this worksheet. Obvious outliers (results that are drastically different from other values) should not be recorded or used in calculations. The average of the test results is calculated then used in the first column (*Test Results* column) on the Advanced Chemical Monitoring Data Sheet.

The data entry screens for Advanced Chemical Monitoring in the Volunteer Monitoring Internet Database (See Chapter 7) are formatted like the Chemical Monitoring Worksheet. The volunteer enters data for the number of replicate samples completed. The database computes the average values and Q-values, then displays the final results in the format of the Water Quality Index data sheet.

How the water quality index (WQI) works

The Advanced Chemical Monitoring Data Sheet on page 75 utilizes a Water Quality Index. The Water Quality Index provides a simple analysis of the results of the eight chemical tests. If you complete at least six of the eight tests, you can derive a <u>single score</u> that will let you know if the stream results are: Excellent, Good, Medium, Bad, or Very Bad for that particular monitoring session. You can also use this value to track changes in your site over time, or compare the quality with other stream sites.

Each of the tests is weighted according to its level of importance to the overall water quality (in this particular index). Dissolved oxygen has the highest weighting factor (0.18); therefore, the oxygen results are the most important value in determining the water quality rating using the index. The weighting scheme allows analysts to condense complex test results into a common water quality measurement that can be readily communicated to the public and to other volunteers. The Water Quality Index score is like a final grade - weighting the results of multiple tests and exams.

How to use the Q-value charts

In order to obtain a WQI Rating, you must first determine the Q-value for each test. After completing a chemical test, use the results to find the Q-value on a Q-chart. Each chemical test has its own Q-chart immediately following the test instructions (pages 43-68). To find the Q-value: locate your test result on the bottom of the appropriate chart (x-axis). Draw a vertical line up from your test result until it intersects the curved line (Q-line). From this point of intersection draw a line across to the left hand side (y-axis). Read the number on the left side of the chart closest to intersection; this is the Q-value for that particular test result. Record the Q-value in the second column of the Advanced Chemical Monitoring Data Sheet. You can also check the Q-value table if your result is close to a given value.

What does a Q-value mean?

You can think of a Q-value as a "Quality-value." It helps interpret your results in terms of the overall health or water quality of your stream. It is like a grade for your stream. The higher the Q-value, the better the test results (100 is the maximum value; 0 is the minimum).

** EXAMPLE **

Date 5-26-04	Chemical Monitoring Work Sheet	Air Temp 2	9.5 °C
Time 1:00pm	Stream Name and Site ID White River Site 0001	Water Temp	22 °c
Current Weather □C	lear/Sunny ☐Overcast ☐Showers ☐Rain (Steady) ☐Storm (Heavy)	Lat	°N
Worst Weather in Past 48 hrs □CI	lear/Sunny ☐Overcast ☒Showers ☐Rain (Steady) ☐Storm (Heavy)	Long	°W

	Units	Comple 1	Sample 2	Sample 2	Averege
	UIIIIS	Sample 1	Sample 2	Sample 3	Average
Dissolved Oxygen (DO)	% Saturation				85%
	mg/L	8.0	7.0		7.5
Avg DO (original)		7.5	7.5	7.5	7.5 ♦
_ DO after 5 days	mg/L	<u> </u>	<u> </u>	<u> </u>	<u>-5.5</u>
BOD 5-day (difference)		1.5	2.5	2.0	2.0
E. Coli Bacteria (purple/blue-violet colonies)	colonies/ 100 mL	215	185		200
General Coliforms (pink/magenta colonies)	colonies/ 100 mL	440	320		380
рН	units	8.0			8.0
Temp at Your Site Upstream (1 mi) Temp	°C	- 22 - 22	22 - 21	22 - 21	22 -21 22
Temperature Change	J	0	1	1	$\frac{21.33}{0.67}$
Orthophosphate	mg/L	0.6			0.6
Total Phosphate (add acid and boil for 30 min)	mg/L	0.06			0.06
Nitrate (NO ₃) (after multiply by 4.4)	mg/L	10.0			10.0
Nitrite (NO ₂) (after multiply by 3.3)	mg/L	0			0
Transparency (from Tube)	cm	25	26	27.5	
Turbidity (from chart – use in database entry)	NTU	30	29	25	28
Ammonia Nitrogen	mg/L				
Other					

Date	Cher	nical N	\onitoring	Work She	et	Air Temp	°C
Time	Stream Name and Site ID					Water Temp °C	
Current Weather Cle Worst Weather in Past 48 hrs	•			(Steady) Storm (I	,	Lat Long	°N
		Units	Sample 1	Sample 2	San	nple 3	Average
Dissolved Oxyge	n (DO)	% Saturation mg/L					 I
Avg DO (origin <u>DO after 5 day</u> BOD 5-day (differ	<u>'S</u>	mg/L			<u>=</u>		<u> </u>
E. Coli Bacteria (purple/blue-violet c	colonies)	colonies/ 100 mL					
General Coliforms (pink/magenta color		colonies/ 100 mL					
рН		units					
Temp at Your — <u>Upstream (1 m</u> Temperature Cha	i) Temp	°C					
Orthophosphate		mg/L					
Total Phosphate (add acid and boil for	or 30 min)	mg/L					
Nitrate (NO ₃) (after multiply by 4.	4)	mg/L					
Nitrite (NO ₂) (after multiply by 3.	3)	mg/L					
Transparency (from	m Tube)	cm					
Turbidity (from char in databas		NTU					
Ammonia Nitroge	n	mg/L					
Other							
Other							
Other							
Other							

Chemical Monitoring Data Sheet (Water Quality Index) Instructions

As you complete each chemical test (or average your results from the Chemical Monitoring Work Sheet), record the values in the first column of the chemical monitoring data sheet.

Test Results				
	7.5	_ mg/L		
Dissolved Oxygen	<u>85</u>	_ % saturation		
E. coli	200	_ colonies/100ml		
рН	8.0	_ units		
B.O.D. 5	2.0	_ mg/L		
H ₂ O Temp Change	0.67	_ change in°C		
Total Phosphate	0.06	_ mg/L		
Nitrate (NO ₃)	10.0	_ mg/L		
Turbidity	28	_ NTU's		

Use the Q-charts or Q-tables in this chapter to derive the Q-values for each test. Record them in the second column.

Test Results						
Dissolved Oxygen	7.5 mg/L 85 % saturation					
E. coli	200 colonies/100ml					
pH	8.0 units 2.0 mg/L					
B.O.D. 5 H ₂ O Temp Change	mg/L 0.67 change in°C					
Total Phosphate						
Nitrate (NO ₃)	mg/L					
Turbidity	28 NTU's					

Q-Value
92
82
<u>80</u> <u>90</u>
<u>98</u> <u>51</u>
53

After the Q-values have been determined and recorded in the second column, multiply the Q-value for each test by the Weighting Factor and record the value in the final Calculation column.

Test Results					
	7.5	mg/L			
Dissolved Oxygen	<u>85</u>	% saturation			
E. coli	200	colonies/100ml			
pH	8.0	units			
B.O.D. 5	2.0	mg/L			
H ₂ O Temp Change	0.67	change in°C			
Total Phosphate	0.06	mg/L			
Nitrate (NO ₃)	10.0	mg/L			
Turbidity	<u>28</u>	NTU's			

Q-Value		Weighting Factor		Calculation
92	Х	.18	=	16.56
<u>37</u>	Х	.17	=	6.29
<u>82</u>	Х	.12	=	9.84
80	Х	.12	=	9.6
90	Х	.11	=	9.9
98_	Х	.11	=	10.78
<u>51</u>	Х	.10	=	<u>5.1</u>
53	Х	.09	=	4.77

Once the calculations are completed for each parameter, you can then sum the Weighting Factor column and the Calculation column. Divide the total of the Calculation column by the total of the Weighting Factor column to obtain the Water Quality Index (WQI).

Excellent 90 - 100% Bad 25 - 50% Good 70 - 90% Very Bad 0 - 25% Medium 50 - 70%

TOTALS 1.0 72.84

WATER QUALITY INDEX RATING GOOD!

If you complete all eight tests, the total of the Weighting Factor column is 1.00 (or 100%). If you are missing one or two tests (but no more than two!) you can calculate an adjusted Water Quality Index (WQI) Rating. Follow the same procedures: Divide the total of the *Calculation* column by the total of the *Weighting Factor* column for the tests you completed to obtain the adjusted WQI.

In the above example, if the Total Phosphate and *E.* coli tests were not completed, the total of the *Weighting Factor* column would be **0.72**, and the total of the *Calculation* column would be **55.77**

Total of Calculation column (Divided by) Total of Weighting Factor column

= Adjusted Water Quality Index Rating

ADVANCED CHEMICAL MONITORING DATA SHEET

Date// Begin Time: (am/pm) # Adults MM DD YY End Time: (am/pm) # Students Certified Monitors' Names Volunteer ID Organization Name Watershed Name						
Stream/River Name(Please do not abbreviate.)	Site ID(Above ID numbers are required.)					
Current Weather	☐ Showers ☐ Rain (Steady) ☐ Storm (Heavy) ☐ Showers ☐ Rain (Steady) ☐ Storm (Heavy)					
WATER QUALITY INDEX (WQI) You may perform as many of the following tests as you wish; however, at least 6 must be completed to obtain a Total Water Quality Index value. Divide the total of the <i>Calculation</i> column by the total of the <i>Weighting Factor</i> column to obtain the Water Quality Index rating.						
Test Results	Q-Value Weighting Calculation Factor					
mg/L Dissolved Oxygen % saturation	X .18 =					
E. coli colonies/100mL	X .17 =					
pH units	X .12 =					
H ₂ O Temp Change change in °C	X .11 =					
Total Phosphate mg/L	X .11 =					
Nitrate (NO ₃) mg/L	X .10 =					
TurbidityNTU's	X .09 =					
	TOTALS					
Excellent 90 - 100% Bad 25 - 49% Good 70 - 89% Very Bad 0 - 24% Medium 50 - 69%	WATER QUALITY					

Water Quality Monitoring Materials

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Catalog # 25001	\$17.50 pkg. of 10	
Catalog # DRP01	\$.12 each (\$1.20 for	
Catalog # DRP03	\$.14 each (\$1.	40 for 10)
h com		
	\$260.00	
		2 years
		6 months
		6 months
2569-49	\$ 13.35	6 months
ey Kit (27120-00):		
24089-32	\$ 7.20	54 months
981-99	\$10.15	60 months
982-99	\$10.15	36 months
987-99	\$15.05	60 months
2125-99	\$21.05	41 months
2449-32	\$ 7.01	60 months
		40 months
		60 months
		60 months
14120-99	\$22.55	25 months
_	4177 00 (100	
	\$175.00 (100)	test tabs)
	\$114.50 (100 :	test tahs)
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		3 years
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Cat #5892	\$14.95	3 years
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^{*} Prices subject to change. Prices shown are for 2002-2003. www.HoosierRiverwatch.com